The Hydration of Sodium Monometaphosphate to Orthophosphate in Varying Concentrations of Hydrogen Ion at 45° Centigrade

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DISSERTATION

Submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy in
the Faculty of Pure Science of
Columbia University.

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BY

SAMUEL J. KIEHL, A. B.

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DEDICATED

TO

LOUELLA SOLLARS KIEHL,

my wife,

whose sympathetic interest has been an inspiration.

ACKNOWLEDGMENT.

THE HYDRATION OF SODIUM MONOMETAPHOSPHATE TO ORTHOPHOSPHATE IN VARYING CONCENTRATIONS OF HYDROGEN ION AT 45° CENTIGRADE.

The hydration of metaphosphoric acid to orthophosphoric acid or a metaphosphate to the orthophosphate, as $NaPO_3 + H_3O \rightarrow NaH_2PO_4$, has attracted the attention of chemists ever since the epochal work of Graham[1]. Much work has been done but the problem is not completely solved. Graham was aware of some of the difficulties to be encountered. In his work he states, "The problem is therefore environed with difficulties." These difficulties seem to be twofold:—First, metaphosphoric acids or their salts are not well understood. It is known that polymers exist the preparation of which has not been thoroughly investigated and the decision as to their forms has been based mainly upon their methods of preparation or empirical formulae rather than upon experimental evidence. Different polymers present different problems of hydration. Second, the rate of hydration must be ascertained by the measurement, at intervals, of either the concentration of the metaphosphate left unchanged in the solution or the concentration of the orthophosphate formed during the progress of the reaction. On account of the widely differing solubilities of the polymeric forms of the metaphosphates, the direct determination involving an actual separation of the orthophosphoric acid from the meta is by no means easy, especially when pyrophosphoric acid is formed as an intermediate product. This separation is actually necessary in order to study the factors influencing the hydration.

So to understand better this reaction the two above mentioned difficulties must be overcome as far as possible. This requires, as a basic consideration, that a definite polymer be prepared and its hydration studied. Furthermore, the definite polymer must be readily and quantitatively separable from the substances formed during the hydration.

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[1] Phil. Trans. **123**, 53 (1833).

Heretofore the methods employed in the study of the hydration of metaphosphoric acid have been mostly indirect, and the acid used was prepared either by dissolving phosphorus pentoxide in cold water or by dehydrating orthophosphoric acid or by preparing a heavy metal salt from which a solution of the meta acid was obtained upon the withdrawal of the metal by hydrogen sulphide. Acidimetry was used by Sabatier[1], Montemartinie and Egid[2], Bertholet and André[3], and Balareff[4]; thermochemistry by Giran[5]; gravimetric analysis by Holt and Meyers[6]; change of index of refraction by Blake and Blake[7]; change of conductivity by Prideaux[8]; and change of the lowering of the freezing point by Holt and Meyers[9].

In their gravimetric method Holt and Meyers precipitated the unchanged metaphosphate in the presence of ortho and pyro as a barium metaphosphate bearing the empirical formula $Ba(PO_3)_2$. By repeated experiments with mixtures of ortho, pyro, and meta they claim very little variation in the composition of their precipitate. However, the result they obtain in the measure of the actual hydration is the best criterion of the trustworthiness of their method. Judging from the irregularity of the curve they publish it seems that their method is open to question or fraught with a considerable error.

Other attempts to apply methods of precipitation were employed to show whether or not pyrophosphoric acid was formed during the process of hydration[10]. Neither method is applicable to the problem. Because on the one hand, the method of Bertholet and André requires the heating of the solution to be analysed acidified with acetic acid on a boiling water bath for three or four hours to secure the formation of an uncertain magnesium ammonium pyro-

[1] Compt. rendu 106, 63 (1888), 108, 734 and 804 (1889).
[2] Gazz. Ital. Chim. 31, I, 394 (1901).
[3] Compt. rendu 124, 261 (1897).
[4] Zeit. Anog. Chem. 72, 85 (1911).
[5] Compt. rendu 135, 1333 (1902).
[6] J. S. C. Trans. 99, 384 (1911).
[7] Am. Chem. J. 27, 68 (1902).
[8] Chem. News 99, 161, (1909).
[9] J. C. S. Trans. 99, 385 (1911), 103, 532 (1913).
[10] Balareff, Zeit. Anorg. Chem. 68, 266 (1910).
    Bertholet and André, Compt. rendu. 124, 261 (1897).

phosphate, — a treatment entirely out of the question in view of the marked effects of temperature and hydrogen ion upon the rate of hydration. On the other hand the precipitation of pyrophosphate of copper or cadmium in an acetic acid solution, the method employed by Balareff, is open to question because upon it he based his contention that no pyrophosphate as an intermediate product was formed during the hydration,— a statement not in harmony with his later work[1].

There have been two different opinions as to whether pyrophosphoric acid was formed as an intermediate product during the hydration of metaphosphoric acid to ortho. One group of chemists maintained that the hydration was direct to ortho, while another claimed pyrophosphoric acid as an intermediate product. The former was supported by Graham[2], Sabatier[3], Montemartini and Egid[4], and Balareff[5]; while Bertholet and André[6], Giran[7], Holt and Meyers[8], and Balareff[9] adhered to the latter.

Accordingly a method has been devised and materials prepared for the attack of this problem whereby the conditions and factors influencing the reaction may be studied to a better advantage by direct standard analytical methods. An account of the investigation will be presented under the following headings: Apparatus, Preparation of Materials, Method of Procedure, Experimental Data, Discussion, and Summary.

[1] Zeit. Anorg. Chem. 96, 103 (1916).
[2] Phil. Trans. 123, 53 (1833).
[3] Compt. rendu. 106, 63 (1888).
[4] Gazz. Ital. Chim. 31, I, 394 (1901).
[5] Zeit. Anorg. Chem. 67, 234 (1909); 68, 288 (1910).
[6] Compt. rendu. 123, 776 (1896); 124, 265 (1897).
[7] J. Russ. Chem. Soc. 30, 99.
[8] J. C. S. Trans. 99, 385 (1911).
[9] Zeit. Anorg. Chem. 96, 103 (1916).

APPARATUS.

Thermostat. A Freas sensitive thermostat was used to maintain a constant temperature for the entire work of hydration and hydrogen ion concentration measurement. By it a constant temperature of 45° C. ± .005 was secured.

Potentiometer. Measurements for the determination of the concentration of hydrogen ion were made with a Leeds and Northrup direct reading potentiometer of low resistance.

Galvanometer. In connection with the potentiometer, a Leeds and Northrup type R, D'Arsonval galvanometer equipped with a telescope and scale was employed. Its resistance was 550 ohms, its sensibility 2000 megohms (5×10^{-10} amp. per mm. at one meter). The period was six seconds, and the critical damping resistance 11,500 ohms.

Standard Cell. A model 4 No. 3921 Weston standard cell served as a basis for all electrical measurements. Its value was 1.01889 volts. This voltage was checked against a cell whose value was checked against a Bureau of Standards standard.

Calomel and Hydrogen Cells and Electrodes. The calomel and hydrogen cells and electrodes employed in the measurement of hydrogen ion concentration were of the type described in the article of Fales and Vosburg[1], excepting a modification of the hydrogen cell by a stopcock on the arm leading to the salt bridge.

Crucible Furnace. All the sodium monometaphosphate was prepared in an electric resistance furnace. It was calibrated for temperature by a thermocouple in such a way that its temperature could be controlled by measurement of the current.

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[1] J. A. C. S. **40,** 1291 (1918).

PREPARATION OF MATERIALS.

MONO-SODIUM PHOSPHATE—$NaH_2PO_4 \cdot 2H_2O$

A quantity of the purest mono-sodium phosphate obtainable was recrystallized three times from distilled water. The precipitation was accomplished each time by adding to the aqueous solution an equal volume of redistilled 95% alcohol and cooling in ice water. The solution was constantly stirred till the precipitation was complete. In this way a very uniform crystalline product was obtained. Upon the addition of the alcohol two liquid phases were formed. As the solid phase appeared the upper liquid phase gradually disappeared till there was but one liquid and one solid phase at complete precipitation. Crystals appeared first at the juncture of the two liquid phases. Attempts to dry the hydrate both by placing it in a desiccator over fused calcium chloride and in an oven at 40° C. proved fruitless. Subsequent analyses for water of hydration from crystals dried in this way gave widely varying results. Hence the drying had to be accomplished in another manner.

The crystals already wet with water and alcohol were washed three times with redistilled alcohol on a Buchner funnel with suction. Then the washing was continued three times with redistilled anhydrous ether. The filter was changed after each ether washing to avoid the retention of water and alcohol by the filter paper. The hydrate was then spread out upon a clean surface and stirred to allow the ether to evaporate. A day for the final drying was selected when the humidity was low. Otherwise the evaporation of the ether would cause a condensation of the moisture in the air upon the surface of the crystals. About fifteen minutes at 20° to 25° C. completed the drying. The hydrate was then kept in a tightly stoppered bottle. Analyses were made on two different lots, one prepared and analysed in March, the other in September with results as follows:

Lot	Sample	Water of hydration plus water of constitution
1	1	34.47%
1	2	34.52%
2	1	34.73%

The theoretical for the hydrate $NaH_2PO_4 \cdot 2H_2O$ is 34.63%. The above figures were obtained by transforming the orthophosphate to the meta according to the method outlined below for the preparation of sodium monometaphosphate.

SODIUM MONOMETAPHOSPHATE—$NaPO_3$.

Sodium monometaphosphate was prepared by dehydrating the $NaH_2PO_4 \cdot 2H_2O$ as above prepared in the electric furnace formerly described in the following manner: The hydrate in a large platinum crucible was held at a temperature of 200° C. for an hour. The temperature was then slowly raised during the next hour till the mass melted to a clear liquid. It was held at this temperature—approximately 600° C.—for ten minutes. The rheostat was set finally so that a temperature of 450° C. was maintained for the next two hours while the substance crystallized. At the end of this crystallization the metaphosphate was quickly cooled by dipping the bottom of the crucible in cold water. About thirty-five grams could be prepared at one time in this way.

The sodium metaphosphate above prepared was investigated by the freezing point method with the following results:

Sodium meta-phosphate in grams	Water in grams	Freezing point depression	Molecular weight
5.0472	100	.916°	102.5
2.8159	100	.546°	95.9
1.3435	100	.351°	86.9

These depressions indicate a sodium metaphosphate whose molecular weight corresponds to the formula $NaPo_3$ (Theoretical—102.04). The above sodium monometaphosphate was formerly prepared in a somewhat similar way[1] from sodium ammonium hydrogen phosphate by heating the resulting vitrious mass from fusion till it crystallized or by slow cooling from fusion. By taking 2.77 grams of their crystals in 100 c. c. of water, Holt and Meyers obtain a depression of .51° which corresponds to a molecular weight of 102 and a formula of $NaPO_3$.

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[1] Tantatar, J. Russ. Phys. Chem. Soc., **30**, 99; Holt and Meyers, J. C. S. Trans. **103**, 535.

An optical study of the sodium monometaphosphate made by Mr. R. J. Colony of the Department of Geology of Columbia University confirms our belief that the sodium monometaphosphate prepared above is a distinct chemical individual. Through the kindness of Mr. Colony we are permitted to publish the following optical properties: It has an index of refraction, $N_g = 1.486 \pm .005$, $N_p = 1.473 \pm .005$, birefringence N_g—$N_p = .013 \pm .005$. It is apparently monoclinic, optically negative and biaxial with a large optical angle. It shows uniformity in behavior, form, and composition.

Sodium monometaphosphate is very soluble in water. It reacts acid to litmus, a three-tenths molar aqueous solution gives a hydrogen ion concentration of 6.5×10^{-7} moles per liter. From a three-tenth molar solution white flocculent precipitates which change to crystalline form on standing, may be obtained from solutions of the nitrates of silver, lead, mercury, and bismuth. With solutions of the nitrates of zinc, cadmium, cobalt, nickel, and copper, white amorphous precipitates are formed. It does not give a precipitate in a solution containing magnesium chloride, ammonius chloride, and ammonium hydroxide in moderately high concentrations, the property employed in the separation of monometaphosphoric acid from orthophosphoric acid.

HYDROCHLORIC ACID.

The hydrochloric acid used was prepared by distilling a constant boiling solution through a quartz condenser. The first and last portions were rejected.

POTASSIUM CHLORIDE.

The calomel cells and salt bridges were prepared from potassium chloride which was purified by recrystallization three times from distilled water and fusion in platinum.

MERCUROUS CHLORIDE.

The mercurous chloride employed to make calomel cells for hydrogen ion measurement was prepared by the electrolytic method of Ellis[1] from mercury redistilled according to Hulett and hydrochloric acid prepared as described above.

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[1] J. A. C. S. **38**, 737 (1916).

MAGNESIA MIXTURE.

The magnesia mixture used was prepared by dissolving 137.5 grams of magnesium chloride, 225 grams of ammonium chloride, and 250 c. c. ammonium hydroxide (specific gravity .9) in 2250 c. c. of water.

METHOD OF PROCEDURE.

In planning a method of procedure the factors influencing the reaction have as far as possible been either measured or controlled. The temperature, the concentration of sodium monometaphosphate, the concentration of orthophosphate, the formation of pyrophosphate, and the concentration of hydrogen ion are the variable factors which influence the hydration of sodium monometaphosphate.

The temperature was regulated and controlled at 45° C. ± .005°. The metaphosphoric acid was separated from the ortho and the amount of the latter determined directly. By difference the unchanged meta was obtained. No satisfactory quantitative method has as yet been found whereby pyrophosphoric acid may be determined in mixtures such as occur in this investigation. So, by other means, an estimate of the amount formed is all that is possible. The concentration of hydrogen ion was measured at intervals during the hydration.

PREPARATION OF SOLUTIONS.

All solutions made up for hydration were prepared at 20° C. The carefully dried and finely pulverized sodium monometaphosphate was weighed and introduced into a volumetric flask. Distilled water was added and the salt completely dissolved. One-half hour was usually required for complete solution at room temperature. The volume was increased till sufficient room was left for the introduction of the required amount of hydrochloric acid used to furnish the hydrogen ion concentration in the particular solution. The acid was the constant boiling mixture previously described whose value had been determined by measuring out 30 c. c. portions by means of a burette and building them up to 1000 c. c. The final acid solutions were titrated with a standard sodium hydroxide solution whose value was gotten by using Bureau of Standards benzoic acid. Phenolphthalein was used as an indicator. As the acid was added the flask was rotated so as to keep from acquiring as little as possible a higher concentration of hydrogen ion in

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any portion of the solution than that ultimately desired. After the introduction of the acid the solution was quickly cooled to 20° C. and the flask filled up to the graduation. After thorough mixing, the solution was put in a "non-sol" bottle and placed in the bath. The whole operation, beginning with the addition of the acid, required not more than ten minutes.

The specific gravity of the solution was taken at 20° C. by means of a Westphal balance at the beginning of the reaction. No change of volume was observed during the hydration greater than one part in one thousand, the precision of the balance[1]. Hence one specific gravity measurement for each solution served as a basis for calculation of the percentage of metaphosphoric acid transformed to the ortho. The concentrations of the solutions were all calculated in moles per liter. Therefore, knowing the specific gravity and the concentration in moles per liter, the amount of sodium monometaphosphate in any weighed quantity of solution could be determined.

THE SEPARATION OF MONOMETAPHOSPHORIC ACID FROM ORTHOPHOSPHORIC ACID.

Monometaphosphoric acid was separated from orthophosphoric acid by means of magnesia mixture in a cold solution. As previously stated, a solution of sodium monometaphosphate does not give a precipitate with magnesia mixture in concentrations used in this procedure and in fact very much higher concentrations. This method of separation has been tested both qualitatively and quantitatively (see Table 1). Seven-tenths of a gram of sodium monometaphosphate together with 25 c. c. of the magnesia mixture prepared above in a total volume of 125 c. c. was allowed to stand twenty-four hours repeatedly and no precipitate appeared while a precipitate of the orthophosphate appeared immediately in another solution similarly treated, excepting that one milligram of phosphorus in the form of orthophosphate was added. It remains now to be shown that monometaphosphoric acid is quantitatively separable from the ortho and that no appreciable hydration occurs during the time of standing required for the precipitation of

[1] Montemartini and Egid, Gazz. Ital. Chim. **31**, I, 394 (1901).

TABLE 1.

Hours stand to ppt	900 mgs. NaPO₃		700 mgs. NaPO₃		500 mgs. NaPO₃		300 mgs. NaPO₃		100 mgs. NaPO₃	
	mgs. P. used in form of PO₄	mgs. P. found in form of PO₄	mgs. P. used	mgs. P. found	mgs. P. used	mgs. P. found	mgs. P. used	mgs. P. found	mgs. P. used	mgs. P. found
12			16.26	16.75						
12			16.61	17.08						
12			16.57	17.28						
12			16.71	17.55						
12			19.80	20.35						
12			19.59	20.06						
12			19.08	19.68						
12			19.74	20.00						
12			39.94	41.53						
12			39.93	41.45						
12			39.90	41.35						
12			39.94	41.40						
12			39.93	41.20						
12			39.93	41.06						
12			16.77	16.75						
6	49.33	51.01	49.33	50.67	49.33	50.06	49.33	49.78	49.33	49.15
12	49.33	*50.42	49.33	50.24	49.33	50.37	49.33	50.09	49.33	49.31
18	49.33	51.15	49.33	51.09	49.33	50.90	49.33	49.85	49.33	49.21

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the magnesium ammonium phosphate. By referring to Table 1 it may be noted that thirty determinations of orthophosphate, according to the method outlined below, in the presence of varying quantities of sodium monometaphosphate from 900 milligrams to 100 milligrams have been made. The amount of orthophosphate used has varied and the time of standing has been 6, 12, and 18 hours respectively. There is an increase in amount found over the amount added which is of the same order irrespective of the time of standing, whether it was 6, 12, or 18 hours. This shows that hydration is not the cause of the increase; for if it were, the amount of increase would be a direct function of the time. The increase seems to be due to absorption of the sodium monometaphosphate by the magnesium ammonium phosphate precipitate, which is subsequently hydrated during the dissolving of the magnesium ammonium phosphate with hot hydrochloric acid. The reaction as will be shown is rapid in a hot acid solution.

The analyses were run in series of five each and the time of standing in the hot acid solution was about the same for all except the one starred in Table 1. This one was re-precipitated immediately and the value of it is smaller than that obtained for both the one that stood six and the one that stood 18 hours in the presence of the same amount of sodium monometaphosphate. At any rate the maximum deviation from the amount used is not greater than .82 of a milligram of phosphorus or 1.5%. From the experimental data below it will be observed that almost all the determinations were made in the presence of much less than 300 milligrams of sodium monometaphosphate where the maximum deviation is in the region of .5 milligram or one per cent.

DETERMINATION OF ORTHOPHOSPHATE.

Orthophosphate was determined by the standard gravimetric method. The samples of the solution were taken by means of Bailey weighing burettes. A standard final volume of 125 c. c. including 25 c. c. of magnesia mixture was used in all determinations. Before precipitation each sample was diluted to 100 c. c. The separation of the magnesium ammonium

phosphate precipitate from the unprecipitated meta was made by filtration not longer than sixteen hours nor less than six hours after the first precipitation. After separation and washing with an ammonium hydroxide-ammonium nitrate solution, the orthophosphate precipitate was dissolved with hot hydrochloric acid, re-precipitated by adding to the solution diluted to 100 c. c. a concentrated ammonium hydroxide solution (sp. gr. .9), 10 c. c. in excess of that required for neutralization. Finally after twelve hours standing the magnesium ammonium phosphate was filtered through a weighed gooch crucible, washed, and ignited and weighed as magnesium pyrophosphate. By this method the amount of the monometaphosphate transformed to ortho could be determined.

FORMATION OF PYROPHOSPHATE.

The analytical results vary somewhat due to the formation of pyrophosphate in the reaction. With no method at present for the separation of pyrophosphoric acid from the ortho except the prevention of its precipitation by an excess of magnesia mixture (magnesium pyrophosphate is soluble in an excess of magnesium salts) at times the ortho precipitate was contaminated a little with it. That there was pyrophosphoric acid formed there was no doubt. The magnesium ammonium phosphate is a definite crystalline product very readily filtered. When pyrophosphate is present these crystals are mixed with a white gelatinous precipitate which is soluble in an excess of magnesium salts. The formation of pyrophosphate was later confirmed by hydrogen ion measurements.

MEASUREMENT OF CONCENTRATION OF HYDROGEN ION.

All hydrogen ion measurements were made at 45° C. by The Saturated Potassium Chloride Calomel Cell method developed in this department[1]. Samples of the solution in process of hydration were taken by means of a pipette and introduced into the hydrogen cell previously steamed and rinsed three times with the solution being measured. After fifteen minutes

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[1] Fales and Mudge, J. A. C. S. **42**, 2434 (1920).

the time required for the system to reach equilibrium, the measurement was made. The hydrogen used was purified by passing it successively through acid permanganate, alkaline pyrogallol, and a portion of the same solution to be measured placed in the thermostat.

The calculations for the molar concentration of hydrogen ion were made by means of the formula,

$$\log C_{H^+} = \frac{A - E}{BT}$$

derived from the Nernst formula.

In this formula C is the concentration of the hydrogen ion in moles per liter, T the absolute temperature, B a constant whose value is .000198 obtained in the transformation of R in the formula used, $E = \dfrac{RT}{nF} \ln \dfrac{C_1}{C_2}$ to volt-coulombs and subsequently dividing by 96,494 coulombs multiplied by the equivalence of hydrogen and the logarithmic modulus .4343 thus fixing its dimensions as volts; E, the observed voltage, and A a constant determined experimentally by measurement of a .0989 M. hydrochloric acid solution whose value was previously checked against Bureau of Standards Benzoic acid. By employing the precentage 91.3%, for a .1 M hydrochloric acid solution determined from the data and curves in the Carnegie Publications for 1907 by Noyes and others, pages 141 and 339, a value of .2356 is obtained whose dimensions are also volts— the theoretical voltage of a one molar hydrogen ion solution for the combination used in this research. The difference in ionization between a .0989 M. and a .1 M. hydrochloric acid solution is less than the experimental error. The formula for 45° C. becomes

$$\log C_{H^+} = \frac{.2356 - E}{.000198 \,(45 + 273)} = \frac{.2356 - E}{.063}$$

EXPERIMENTAL DATA.

The following table outlines the plan adopted in securing experimental data on hydration of solutions of different hydrogen ion and monometaphosphate concentrations.

TABLE 2.
Solutions studied.

Solution	Conc. NaPO$_3$ moles per liter at 20° C.	Conc. HCl moles per liter at 20° C.	Specific gravity at 20° C.
C	.5	.483	1.045
D	.5	.483	1.044
G	.5	.339	1.041
E	.5	.339	1.042
B	.5	.192	1.042
H	.5	.192	1.041
K	.3	.339	1.025
M	.3	.339	1.026
N	.1	.339	1.011
O	.1	.339	1.011
Z	.3	.010	1.025
Z A	.3	.010	1.025
S	.3	.000	1.025
S A	.3	.000	1.025

From the outline it will be observed that hydrations were run in duplicate with the exception of the last four. Duplicate samples of the latter were taken as shown by tables which follow.

The hydration and hydrogen ion concentration tables of solutions C, G, B, M, and N which are duplicates of D, E, H, K, and O respectively have been omitted. The mean deviation of the results in duplicates is not greater than five per cent when the concentration of pyrophosphate is high at the beginning nor greater than one per cent. when the hydration nears completion.

TABLE 3.

Hydration in Solution D.

Concentration $NaPO_3 = -5$ M. at 20° C.
Temperature $= 45°$ C.
Concentration $HCl = .483$ M. at 20° C.
Specific Gravity $= 1.044$ at 20° C.

No. of sample	Time hrs. min.	Total Phosphorus in mgs.	Phosphorus as ortho in mgs.	Percentage hydrated
1	1 :45	89.61	7.41	8.27
2	4 :40	79.14	37.32	47.13
3	10 :40	78.30	51.71	65.99
4	24 :10	79.37	64.81	81.59
5	48 :25	78.60	69.15	87.93
6	72 :55	79.84	74.20	92.66
7	120 :10	78.89	76.37	96.74
8	168 :42	74.42	73.31	98.44
9	252 :10	78.15	79.16	101.20

This table furnishes the data for the curve in figure 1.

TABLE 4.

Hydrogen Ion Concentration during Hydration in Solution D.

No. of sample	Time hrs. min.	Voltage	Concentration in moles per liter
1	1 :00	.2667	.3209
2	5 :15	.2793	.2024
3	11 :30	.2838	.1717
4	25 :15	.2874	.1506
5	49 :00	.2924	.1255
6	74 :25	.2957	.1112
7	121 :25	.2977	.1033
8	170 :00	.3022	.0877
9	243 :00	.2995	.0968
10	152 :00	.2995	.0968

This table furnishes the data for the curve in figure 1.

TABLE 5.

Concentration of $NaPO_3 = .5$ M. at 20º C.
Temperature $= 45º$ C.
Concentration of HCl $= .339$ M. at 20º C.
Sp. Gr. $= 1.042$ at 20º C.

No. of sample	Time hrs. min.	Total Phosphorus in mgs.	Phosphorus as ortho in mgs.	Percentage hydrated
1	2:10	151.09	11.43	7.56
2	5:10	77.36	19.96	25.80
3	11:10	77.42	38.91	50.26
4	23:10	76.37	51.48	67.41
5	48:35	78.02	58.59	75.10
6	71:25	80.03	65.95	80.53
7	119:03	78.42	66.09	84.28
8	166:59	72.98	66.45	91.05
9	239:25	77.14	73.84	95.72
10	383:25	86.54	87.16	102.80

This table furnishes the data for the curve in figure 1.

TABLE 6.

Hydrogen Ion Concentration during Hydration in Solution E.

No. of sample	Time hrs. min.	Voltage	Concentration in moles per liter
1	1:35	.2823	.1815
2	5:45	.2950	.1140
3	10:55	.3004	.0936
4	24:10	.3082	.0704
5	47:20	.3138	.0574
6	72:55	.3174	.0503
7	120:10	.3216	.0434
8	167:45	.3242	.0392
9	240:40	.3276	.0347
10	384:25	.3276	.0347

This table furnishes the data for the curve in figure 1.

TABLE 7.

Hydration in Solution H.

Concentration of $NaPO_3 = .5$ M. at 20° C.
Temperature $= 45°$ C.
Concentration of HCl $= .192$ M. at 20° C.
Sp. Gr. $= 1.041$ at 20° C.

No. of sample	Time hrs. min.	Total Phos- phorus in mgs.	Phosphorus as ortho in mgs.	Percentage hydrated
1	6:12	157.33	21.74	13.82
2	13:22	78.80	23.22	29.47
3	23:29	77.28	34.70	44.91
4	35:57	84.62	Sample lost in filtration	
5	47:17	83.33	52.82	63.38
6	71:12	81.57	56.42	69.16
7	119:19	59.59	59.59	73.40
8	167:36	75.55	60.88	80.58
11	192:32	77.12	60.23	78.11
12	215:18	79.55	65.42	82.42
13	263:42	78.28	66.65	85.13
14	335:42	79.63	68.29	85.76
15	457:07	85.64	79.08	92.34
16	678:36	79.46	76.29	96.01
17	875:18	67.23	66.17	98.43
18	875:18	94.86	93.29	98.36

This table furnishes the data for the curve in figure 1.

TABLE 8.

Hydrogen Ion Concentration during Hydration in Solution H.

No. of sample	Time hrs. min.	Voltage	Concentration in moles per liter
1	1:17	.2960	.1101
2	5:55	.3147	.0555
3	13:30	.3220	.0425
4	24:30	33.13	.0303
5	36:30	.3361	.0254
6	48:15	.3386	.0231
7	71:57	.3424	.0202
8	120:25	.3487	.0160

TABLE 8—Continued.

9	168:17	.3522	.0141
10	193:25	.3533	.0135
11	216:04	.3539	.0133
12	264:34	.3563	.0121
13	337:00	.3580	.0114
14	457:48	.3590	.0110
15	673:10	.3614	.0100
16	876:12	.3630	.0095

This table furnishes the data for the curve in figure 1.

TABLE 9.

Hydration in Solution K.

Concentration of $NaPO_3$ = .3 M. at 20º C.
Temperature = 45º C.
Concentration of HCl = .339 M. at 20º C.
Sp. Gr. = 1.025 at 20º C.

No. of sample	Time hrs. min.	Total Phosphorus in mgs.	Phosphorus as ortho in mgs.	Percentage hydrated
1	1:30	190.96	17.64	9.24
2	3:00	146.91	53.08	36.05
3	7:00	97.77	57.50	58.82
4	15:00	61.37	40.00	65.17
5	27:00	79.75	58.65	73.54
6	51:00	72.86	62.83	86.22
7	83:25	93.01	87.33	93.89
8	120:10	50.88	49.00	96.31
9	168:25	49.18	47.91	97.44
10	240:01	46.05	45.41	98.60

This data furnishes the data for the curve in figure 2.

TABLE 10.

Hydrogen Ion Concentration during Hydration in Solution K.

No. of sample	Time hrs. min.	Voltage	Concentration in moles per liter
1	1:10	.2781	.2115
2	3:10	.2808	.1917
3	7:55	.2858	.1597

TABLE 10—Continued

4	14:50	.2884	.1452
5	24:31	.2929	.1232
6	50:05	.2953	.1128
7	83:55	.2969	.1064
8	120:44	.3012	.0909
9	169:00	.2997	.0961
10	194:26	.2992	.0978
11	242:00	.2992	.0978
12	250:53	.3018	.0900
13	335:07	.3006	.0930
14	365:45	.3007	.0926

This data furnishes the data for the curve in figure 2.

TABLE 11.

Hydration in Solution O.

Concentration of $NaPO_3 = .1$ M. at 20^0 C.
Temperature $= 45^0$ C.
Concentration of $HCl = .339$ M. at 20^0 C.
Sp. Gr. $= 1.011$ M. at 20^0 C.

No. of sample	Time hrs. min.	Total Phosphorus in mgs.	Phosphorus as ortho in mgs.	Percentage hydrated
1	1:30	97.86	11.33	11.83
2	3:00	61.70	25.95	42.06
3	7:10	64.07	44.26	69.08
4	13:10	63.53	50.26	79.10
5	24:10	70.02	61.85	88.34
6	47:40	61.67	59.34	96.22
7	72:10	62.90	61.63	97.89

This table furnishes the data for the curve in figure 3.

TABLE 12.
Hydrogen Ion Concentration during the Hydration in Solution O.

No. of sample	Time hrs. min.	Voltage	Concentration in moles per liter
1	1:00	.2715	.2702
2	3:45	.2714	.2702
3	7:15	.2734	.2522
4	13:40	.2732	.2530
5	24:50	.2751	.2361
6	49:00	.2764	.2251
7	72:53	.2760	.2284

This table furnishes the data for the curve in figure 3.

TABLE 13.
Hydration in Solution Z and Z A.

Concentration of $NaPO_3 = .3$ M. at 20° C.
Temperature $= 45°$ C.
Concentration of HCl $= .01$ M. at 20° C.
Sp. Gr. $= 1.022$ at 20° C.

No. of sample	Time hrs. min.	Total Phosphorus in mgs.	Phosphorus as ortho in mgs.	Percentage hydrated
1-Z-A	166:15	190.36	23.41	12.30
2-Z-A	166:15	196.32	23.58	12.01
3-Z-A	333:00	165.99	42.51	25.34
4-Z-A	333:00	191.81	....	....
5-Z-A	501:00	148.31	64.64	43.60
6-Z-A	501:00	139.51	56.14	40.30
7-Z	665:00	92.31	44.88	48.61
8-Z	665:00	98.34	47.61	48.41
9-Z	952:30	87.05	51.15	58.75
10-Z	952:30	99.95	57.53	57.57
11-Z	1386:45	89.21	65.14	73.02
12-Z	1386:45	101.11	73.61	72.81
13-Z	2248:30	94.96	82.65	87.03
14-Z	2248:30	103.65	88.72	87.58
15-Z	2944:45	75.06	70.07	93.35
16-Z	2944:45	66.49	61.93	93.15
17-Z	3469:20	79.87	77.43	96.95
18-Z	3469:20	72.21	70.73	97.14

This table furnishes the data for the curve in figure 4.

TABLE 14.

Hydrogen Ion Concentration during the Hydration in Z.

No. of sample	Time hrs. min.	Voltage	Concentration in moles per liter
1	0:40	.3637	.009477
2	7:45	.3777	.005552
3	19:45	.3829	.004591
4	44:00	.3896	.003594
5	72:20	.3960	.002844
6	120:20	.4039	.002131
7	167:41	.4089	.001841
8	480:03	.4258	.000957
9	953:38	.4393	.000584
10	1553:45	.4455	.000466
11	2946:03	.4507	.000384
12	3570:47	.4524	.000362

This table furnishes the data for the curve in figure 4.

TABLE 15.

Hydration in Solution S and S-A.

Concentration $NaPO_3$ = .3 M. at 20° C.
Temperature = 45° C.
Concentration HCl = 0.
Sp. Gr. = 1.022 at 20° C.

No. of sample	Time days	Total Phosphorus in mgs.	Phosphorus as ortho in mgs.	Percentage hydrated
1-S-A	25	621.02	11.21	1.81
2-S-A	25	593.65	10.62	1.79
3-S-A	45	448.48	23.80	5.31
4-S-A	45	443.94	22.09	5.00
5-S	60	232.07	17.31	7.46
6-S	60	240.47	18.20	7.56
7-S	74	132.17	13.77	10.42
8-S	74	152.78	15.89	10.40
9-S	88	115.72	15.22	13.15
10-S	88	118.56	15.80	13.33
11-S	109	99.44	19.54	19.65
12-S	109	90.76	17.67	19.47

TABLE 15—Continued.

13-S	149	91.92	29.80	32.42
14-S	149	99.52	32.00	32.23
15-S	177	98.02	40.56	41.37
16-S	177	98.13	40.67	41.44
17-S	200	99.83	47.91	49.11
18-S	200	99.21	48.28	49.16

This table furnishes the data for the curve in figure 5.

TABLE 16.

Hydrogen Ion Concentration during Hydration in Solution S.

No. of sample	Time hrs. min.	Voltage	Concentration x 10^6 in moles per liter
1	1:30	.6252	.65
2	4:30	.6234	.70
3	10:48	.6195	.81
4	23:00	.6070	1.27
5	48:30	.5900	2.37
6	72:00	.5798	3.44
7	96:00	.5636	6.22
8	199:15	.5679	5.31
9	216:50	.5641	6.11
10	289:43	.5565	8.06
11	343:37	.5555	8.36
12	480:36	.5449	12.30
13	602:45	.5406	14.52
14	724:45	.5373	16.68
15	890:45	.5339	18.41
16	1158:40	.5284	22.51
17	1494:33	.5248	25.68
18	2183:50	.5209	29.61
19	4799:28	.5109	41.80

This table furnishes the data for the curve in figure 5.

TABLE 17.

The Concentration of Hydrogen Ion in Monosodiumphosphate
Hydrochloric Acid Solutions.

(The solutions were made up at 20° C. and measured at 45° C.)

Concentration HCl Moles per liter at 20° C.

Concentration NaH$_2$PO$_4$ Moles per Liter	0		.1		.2	
	voltage	Con. H$^+$x10^4	voltage	Con. H$^+$	voltage	Con. H$^+$
0	....	....	.3013	.0906	.2834	.1743
.1	.5225	.2793	.3336	.0278	.2979	.1026
.2	.5172	.3390	.3624	.0097	.3190	.0474
.3	.5126	.4014	.3772	.0057	.3398	.0221
.4	.5085	.4659	.3874	.0039	.3537	.0133
.5	.5049	.5313	.3949	.0039	.3638	.0092

Concentration HCl Moles per liter at 20° C.

Concentration NaH$_2$PO$_4$ Moles per Liter	.3		.4		.5	
	voltage	Con. H$^+$x10^4	voltage	Con. H$^+$	voltage	Con. H$^+$
0	.2719	.2653	.2630	.3674	.2595	.4176
.1	.2790	.2047	.2683	.3027	.2599	.4114
.2	.2932	.1241	.2774	.2170	.2670	.3162
.3	.3105	.0647	.2889	.1426	.2753	.2343
.4	.3262	.0352	.3026	.0864	.2858	.1597
.5	.3389	.0229	.3175	.0501	.2969	.1064

The data in this table serve as a basis for plotting curves
in figure 6.

TABLE 18.

**Concentration of Hydrogen Ion in Sodium Bi-pyrophosphate
Hydrochloric Acid Solution.**

(The solutions were made at 23° C. and measured at 45° C.)

Concentration HCl Moles per liter.

		.192		.339		.483	
		voltage	Con. H⁺	voltage	Con. H⁺	voltage	Con. H⁺
	.01	.2820	.1834	.2656	.3340	.2562	.4710
	.05	.2910	.1320	.2722	.2625	.2595	.4175
Concentration Na₂H₂P₂O₇ Moles per Liter	.10	.2981	.1019	.2755	.2326	.2624	.3755
	.15	.3055	.0777	.2791	.2039	.2655	.3353
	.20	.3130	.0591	.2822	.1821	.2680	.3060
	.25	.3197	.0462	.2880	.1473	.2695	.2898

To obtain the $Na_2H_2P_2O_7$, the normal sodium pyrophosphate was used and additional HCl to that indicated in Table 18 was added so that the ratio of two moles of HCl to one mole of $Na_4P_2O_7$ was maintained in each solution in excess of that tabulated. The data in this table serve as a basis for plotting curves in figure 8.

DISCUSSION

CHANGE OF CONCENTRATIONS OF HYDROGEN ION.

A comparison of the data from the various solutions studied reveals the great influence hydrogen ion has upon the hydration of sodium monometaphosphate. By the direct method employed it was possible to add hydrogen ion and determine its influence. The experimental data in the tables above and the curves in figures 1, 2, 3 and 4 show how the hydrogen effects the rate of hydration and how there is a progressive decrease of hydrogen ion during the reaction. This decrease is very readily explained by the withdrawal of hydrogen ion by the less dissociated ortho and pyrophosphoric acids formed in the reaction. In tables 17 and 18 and curves in figures 6 and 8 it is shown that there is a gradual lowering of the hydrogen ion concentration by increasing both the ortho and pyrophosphate concentrations separately. In all solutions studied this decrease of hydrogen ion has been evident except in solution S tables 15 and 16 and figure 5 where there was an actual increase. This change in the hydrogen ion concentration is markedly pronounced even when our method showed very little or no orthophosphate in solution after considerable time. This is shown in curves of figures 1, 2, 3, 4 and 5.

PERIOD OF APPARENT INHIBITION.

In figures 1, 2, 3, 4 and 5 all hydration curves show periods of apparent inhibition. In hydration curves D, E and H of figure 1, K of figure 2, and O of figure 3 these periods are one hour, one hour thirty minutes, six hours, two hours, and one hour thirty minutes respectively. During this apparent inhibition there is a rapid decrease of hydrogen ion which cannot be accounted for by the decrease caused by the presence of sufficient orthophosphate in solution at that time. Even after the ortho has acquired a comparatively high concentration the decrease is not accounted for by it. For example in figure 1, curve H, there is a decrease of .14 mole of hydrogen ion with the for-

Hydration and hydrogen Ion Concentration
Curves of Solutions D, E and H.
Against Time

D = .5 M. Na PO₃ & .483 M. HCl
E = .5 M. Na PO₃ & .339 M. HCl
H = .5 M. Na PO₃ & .192 M. HCl
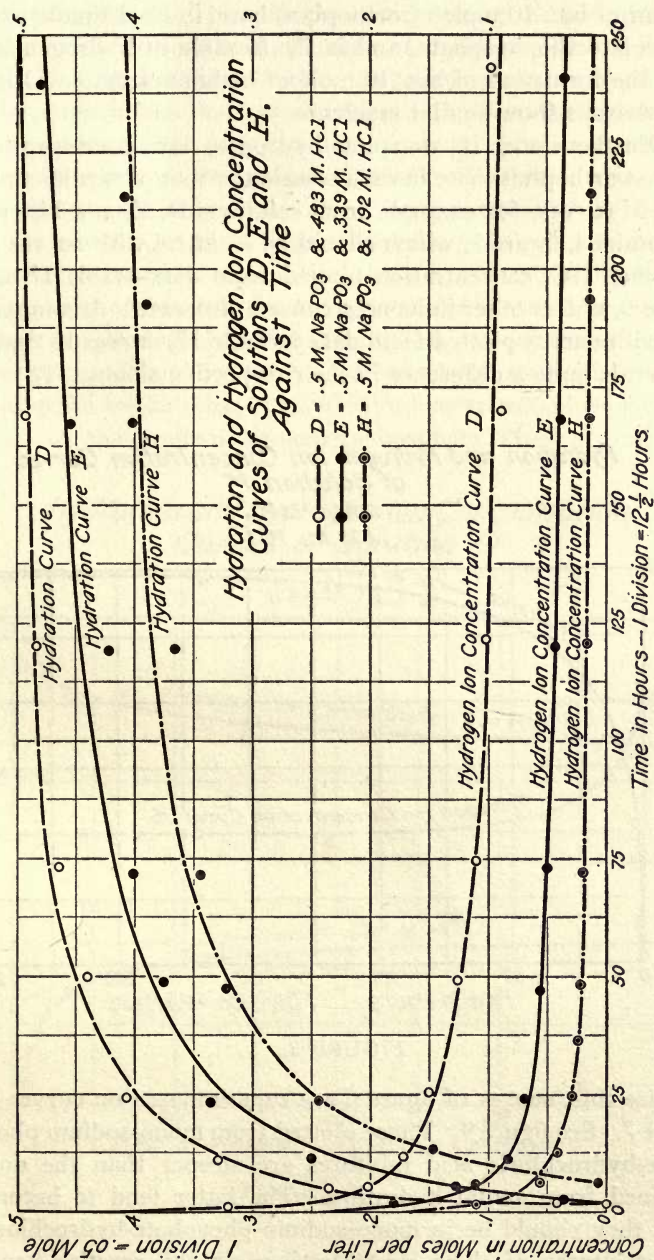
Time in Hours—1 Division = 12½ Hours

FIGURE 1.

mation of but .10 mole of orthophosphate, in E, .13 mole with .10 mole orthophosphate, and in C, .16 mole of hydrogen ion with the formation of but .10 mole of orthophosphate. Other comparisons show similar results.

Furthermore, if we plot hydrogen ion concentration against orthophosphate in each solution at that particular time, a set of curves, for example from solutions D, E, and H, may be obtained, figure 7, which should be identical with curves of the same HCl concentration plotted from data—table 17 and figure 6, unless other influences cause a decrease. A comparison with curves plotted from data in table 17, curves in figure 6, reveals quite a difference in their respective slopes. To em-

Hydration and Hydrogen Ion Concentration Curves of Solution K
.3 M. NaPO₃
.339 M. HCl
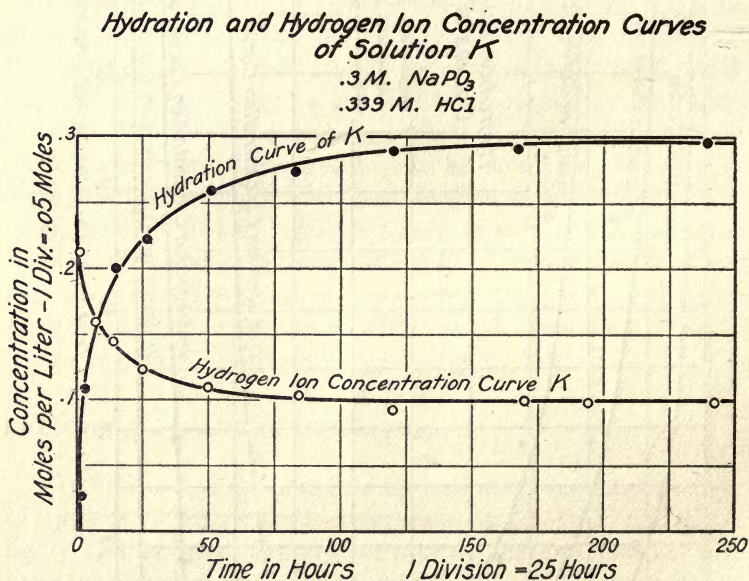
FIGURE 2.

phasize this, curves of figure 6 are superimposed on curves of figure 7. See figure 9. Those plotted from mono-sodium phosphate-hydrochloric acid mixtures are steeper than the ones obtained from actual hydration. The latter tend to become what they should be in mono-sodium phosphate-hydrochloric acid mixtures of their concentrations as the reaction tends

toward completion. There is, therefore, during the period of apparent inhibition a rapid decrease of hydrogen ion—a reaction which requires time. Also, the concentration of hydrogen ion is much less than we should expect normally in solutions of hydrochloric acid and mono-sodium phosphate mixtures of the same concentration, figure 9. Furthermore such differences are not caused by sodium monometaphosphate, because the reaction requires time. Experience has shown that such an adjustment of equilibrium would be attained by the time the solution reached the temperature of the bath or one-half hour provided no change in the polymeric condition of sodium monometaphosphate occurs. It has been shown by the freezing point method that in solution sodium trimetaphosphate changes to the sodium monometaphosphate after a time[1].

Hydration and Hydrogen-Ion Concentration Curves of Solution O
.1 M. Na PO₃
.339 M. HCl
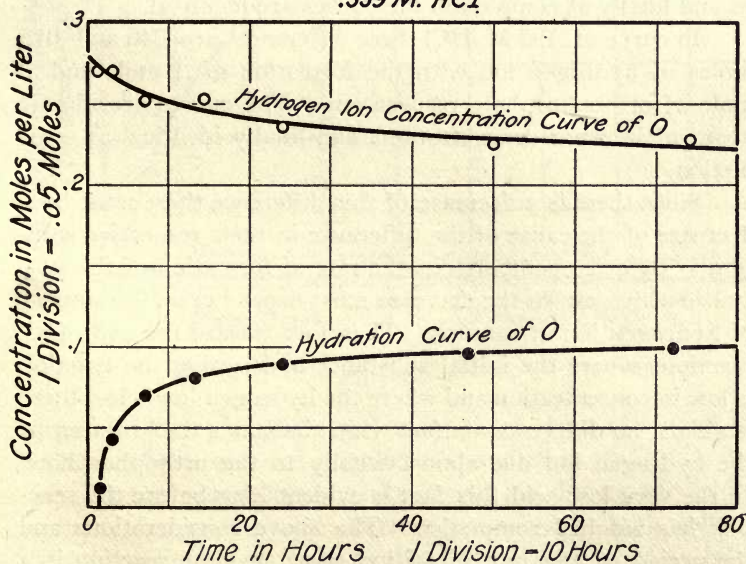
FIGURE 3.

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[1] Holt and Meyers J. C. S., Trans. **103**, 1913, 532.

That there is no change is shown by the preparation of a hydrate of sodium monometaphosphate, where the solution was concentrated till it separated. It is the hydrate of sodium monometaphosphate we obtain as its solution behaves like the original solution. Therefore it does not seem that the decrease of hydrogen ion can be caused by the unchanged monometaphosphate. By comparing curves made from actual mixtures with those made from data obtained from hydration with the same hydrochloric acid concentrations in figure 9, a difference in curve .483 M. HCl of .11 mole of hydrogen ion occurs when .1 mole of orthophosphate is formed, .07 with .2 mole of orthophosphate, .02 mole with .3 mole of orthophosphate, .01 mole with .4 mole of orthophosphate, and finally when the reaction is complete the difference has disappeared. In curves .339 M. HCl there is a difference of .1 mole hydrogen ion when .1 mole orthophosphate is formed, .07 mole when .2 mole orthophosphate is formed, and .024 mole when .3 mole of orthophosphate is formed, .008 mole when .4 mole of orthophosphate is formed and finally at completion the curves are identical.

In curve of .192 M. HCl these differences are .046 and .015 moles of hydrogen ion with the formation of .1 mole and .2 mole of orthophosphate respectively. The curves are almost identical in other concentrations and finally identical at completion.

Since there is a decrease of this difference there must be a decrease of the cause of the difference in their respective solutions. By cross comparisons the rate of formation of the substance which causes the decrease must depend upon the amount of hydrogen ion in solution. Therefore toward the end of all reactions where the initial substance undergoing the reaction is low in concentration and where the hydrogen ion is low there is almost no difference—a fact which indicates the lowering of the hydrogen ion due almost wholly to the orthophosphate. In the very low acid this fact is evident long before the reaction has reached completion. The above considerations and the period of apparent inhibition show that the reaction is a two stage reaction where the first stage decreases and the last stage overtakes it. Then too the difference in higher concentrations of hydrogen ions does not finally disappear until the

reaction is almost complete. This indicates that hydrogen ion has more effect upon the first stage of the reaction than the last stage. These comparisons were made in .5 molar solutions. Similar results are obtainable from other solutions.

Now since pyrophosphate was actually formed during the analysis of orthophosphate and since in table 18 measurements of hydrogen ion have been made in solutions of hydrochloric acid-pyrophosphate mixtures and curves plotted in figure 8 which show the decrease of hydrogen ion with an in-

Hydration and Hydrogen Ion Concentration Curves of Solutions Z & Z-A
.3 M. Na PO₃
.01 M. HCl
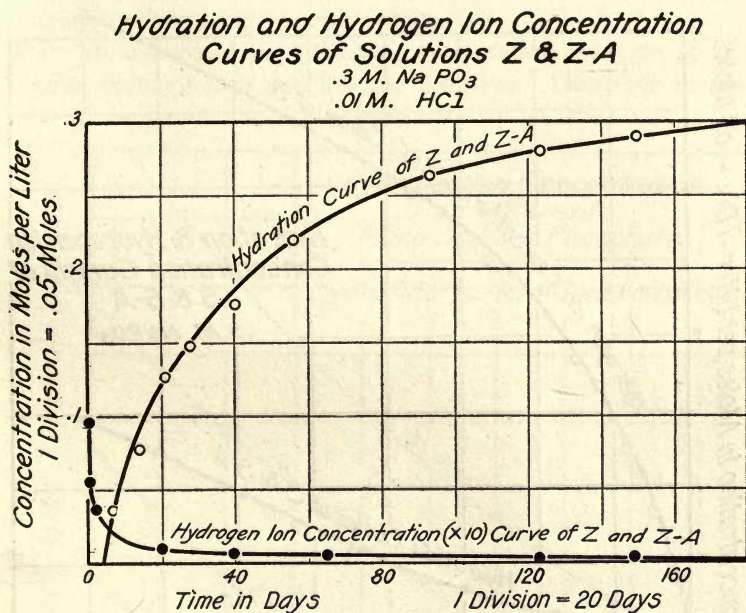
FIGURE 4.

crease of pyrophosphate and since there is an abnormal decrease in hydrogen ion in solutions studied excepting S, it is evident that the decrease of hydrogen ion during the hydrations is due to the joint effect of pyro and orthophosphates, and from the above it seems that pyro is formed as an intermediate product. From figures 6, 7, 8 and 9, an estimate of the amount of pyrophosphate formed may be made by approximating the amount of pyro necessary to cause the ab-

normality of the various curves in figure 9. In solution C, .5 M. $NaPO_3$ and .483 M. HCl there is the greatest deviation. From the difference of hydrogen ion concentration there is at least .1 M. of $Na_2H_2P_2O_7$ (the intermediate product) formed as a maximum. Then there are all the possible concentrations existing in the solution between this upper limit and zero as the difference in hydrogen ion becomes progressively less. Other solutions show a lower value for their upper limits depending on the initial acid and $NaPO_3$ concentrations.
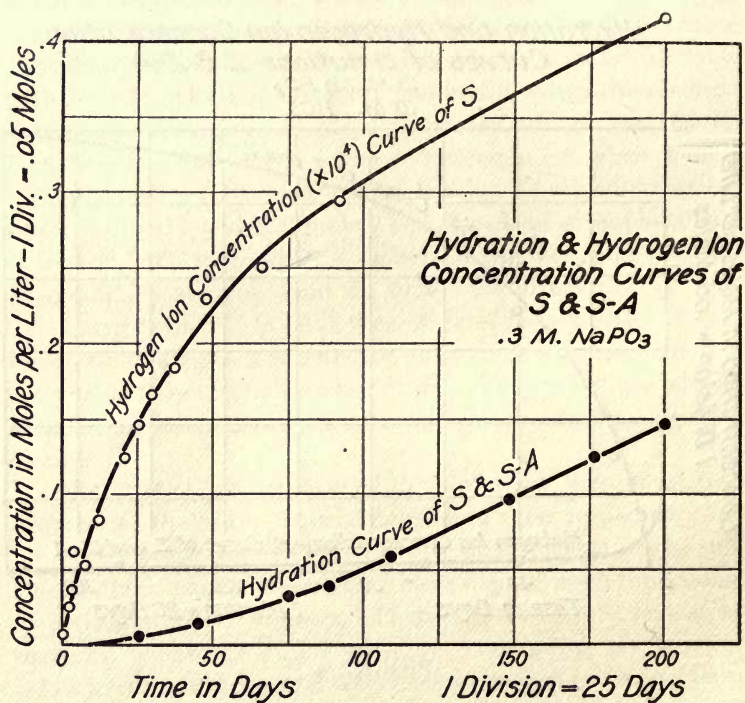
FIGURE 5.

Now as to the period of apparent inhibition, it is not likely that if pyrophosphoric acid is formed as an intermediate product, that the hydration of pyro to orthophosphate would be delayed while the pyro built to a certain concentration before it began the second stage of the reaction. It seems rather that the reaction would begin just as soon as we had the slightest

trace of pyro in solution. In other words at the beginning of the final stage of the reaction the velocity would be zero while the initial velocity of the first stage would be a maximum. Therefore if there is any hydration at all in the final stage the velocity must rise to a maximum and decrease to zero at completion. The maximum for any particular solution would be when the relative influence of the hydrogen ion, which is decreasing, is counteracted by the pyrophosphate and orthophosphate formed. There are two tendencies,—one to slow up the velocity by the withdrawal of hydrogen ion, the other to speed it up by increasing pyrophosphate.

It is evident then that the acceleration must be positive, pass through zero and become negative. This then means a
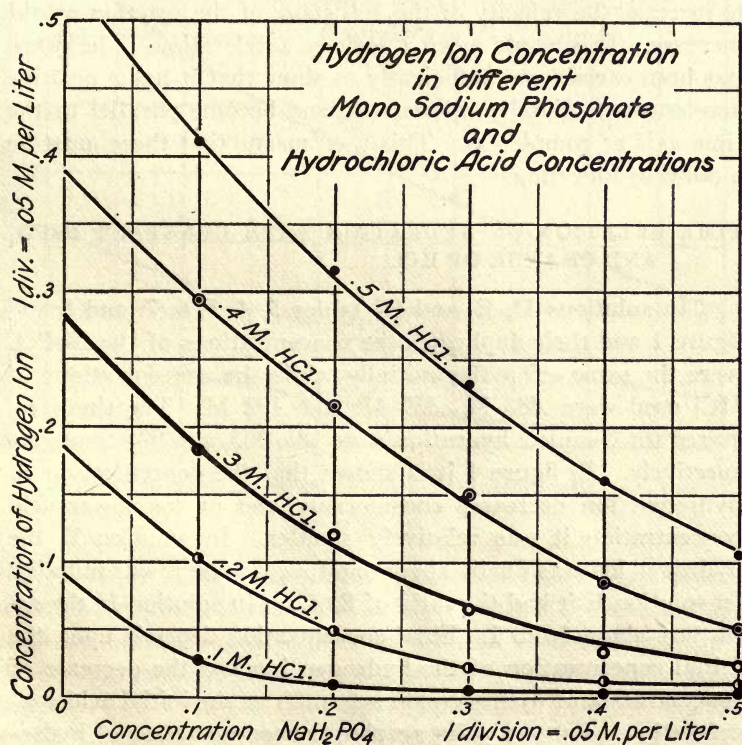
FIGURE 6.

point of inflection near the beginning in all the hydration curves. In solution S, figure 5, it has been experimentally shown that there should be a point of inflection because the hydration curve is concave toward the time axis. In other curves where the reactions were so rapid it was impossible to secure reliable data near the beginning. In S since these reactions are consecutive and since we started with very low hydrogen ion concentration and since by former hydrations we know the accelerating effect of hydrogen ion upon the first stage of the reaction and since we have shown by measurement that the concentration of hydrogen ion increases in S we may therefore conclude that as the concentration of hydrogen ion increases the concentration of the pyrophosphate would tend to increase and as the concentration of the pyrophosphate tends to increase the velocity of the last stage of the reaction would increase. This would mean a positive acceleration. The curve has been carried out sufficiently to show that it has a positive acceleration. Finally this curve must become parallel to the time axis at completion. This then means that there must be a point of inflection.

TIME RELATION OF HYDRATION WITH CONSTANT NaPO$_3$ AND CHANGE OF HCl.

In solutions D, E, and H, tables 3, 4, 5, 6, 7, and 8 and figure 1 and their duplicates the concentrations of the NaPO$_3$ were the same, .5 molar initially while the concentrations of HCl used were .483 M. .339 M. and .192 M. The times required for complete hydration were 185, 365, and 975 hours respectively. In figure 1 it is shown that the concentration of hydrogen ion decreases considerably and in the lower acid concentration it was relatively smaller. In solution D the hydrogen ion was finally about one-fourth what it was initially. In solution E it had the ratio of 8 to 1. In solution H the ratio was about 16 to 1. Final concentration depends upon the initial concentration of the hydrogen ion and the decrease of concentration of hydrogen ion is greater as the initial acid concentration is less to a point nearing the concentration of hydrogen ion furnished by a monosodium phosphate solution of the same molar concentration, the final product of the reaction.

In solutions K, Z, and S the initial concentration of NaPO₃ was .3 molar and the concentration of HCl in each case was .339 M., .010 M., and 000M. The times required for complete hydration were 260 hours, 175 days, and at the end of 200 days S was 49.14% hydrated. At a point where the velocity was at maximum in S figure 5 it would have required 357 days to complete the reaction had it continued uniformly from that point to completion. So at a minimum it would require at least a year for complete hydration of a .3 molar aqueous solu-
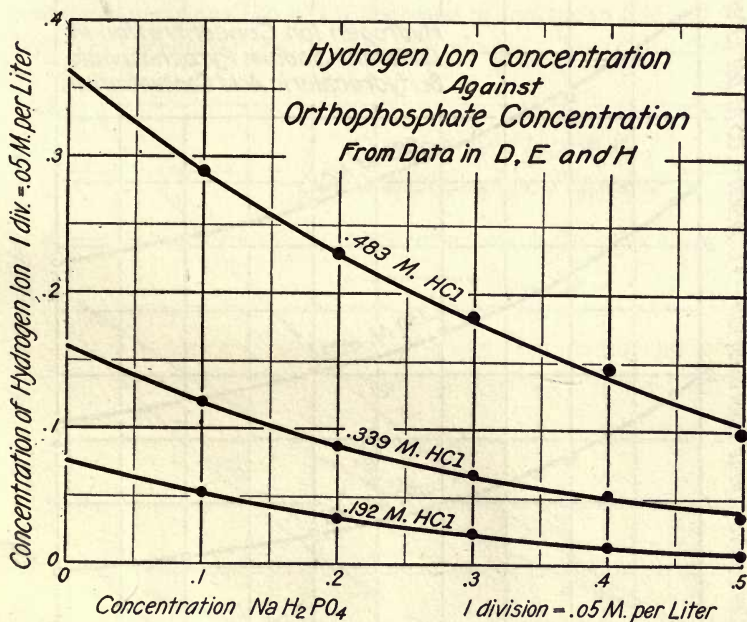
FIGURE 7.

tion at 45° C. It is quite probable however that several years would be required because the velocity gradually decreases as the reaction nears completion. In solution K figure 2 the hydrogen ion concentration was about two-fifths of what it was initially. The ratio in solution Z was 26 to 1, figure 4. In solution S at the end of 200 days there was an actual increase of hydrogen ion concentration which was progressive with time. The ratio of the initial concentration to the final meas-

urement at the end of 200 days was 1 to 65. The concentration of the hydrogen ion is 65 times greater at the end of 200 days than at the beginning. It may be pointed out here too that the concentration of hydrogen ion at this point is considerably greater than the concentration of hydrogen ion in a solution of mono-sodium phosphate of the same concentration—the final product of the hydration. The concentration measured at the end of 200 days was 4.18×10^{-5}, table 16, while that in a
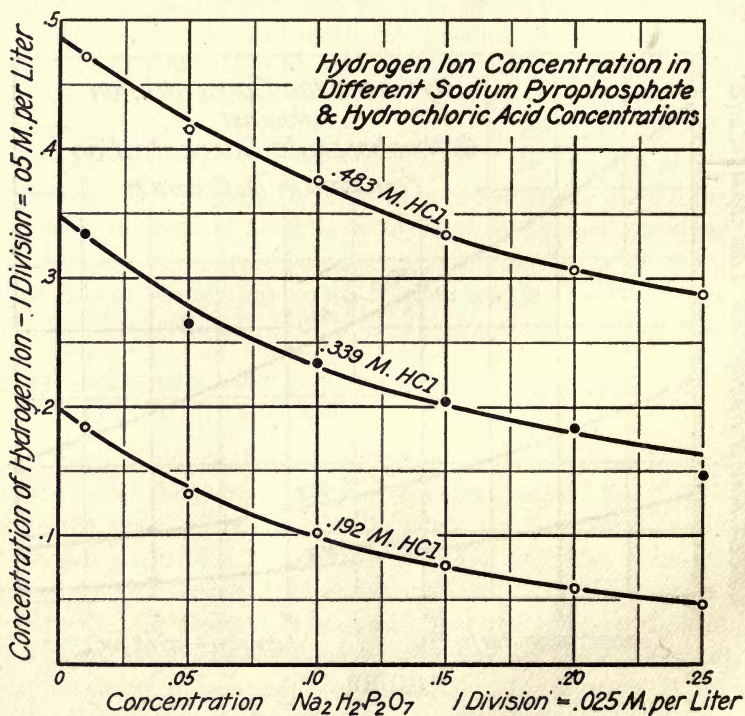

FIGURE 8.

.3 M. NaH_2PO_4 is only 4.01×10^{-5}, table 17. Now since we would expect a hydrogen ion concentration of 4.01×10^{-5} from a .3 Molar aqueous solution of $NaPO_3$ when it is completely hydrated, this is another indication that pyrophosphate is formed as an intermediate product. It would indicate that this hydrogen ion concentration in S should go through a maximum.

This may be explained from the pyrophosphate formed in the solution. From the third ionization constant determined recently[1] we obtain an hydrogen ion concentration of 1×10^{-4} moles per liter for a .3 M. $Na_2H_2P_2O_7$ solution. By actual measurement at 45° C. of .2 molar solution 1.71×10^{-4} is obtained, a concentration four times as great as the last concentration measured in solution S. Furthermore for a given initial concentration of sodium monometaphosphate there should be an initial concentration of hydrogen ion which would remain invariable throughout the entire hydration, because in higher acid concentrations there is a decrease of hydrogen ion and in very low concentrations there is an increase. Therefore there

FIGURE 9.

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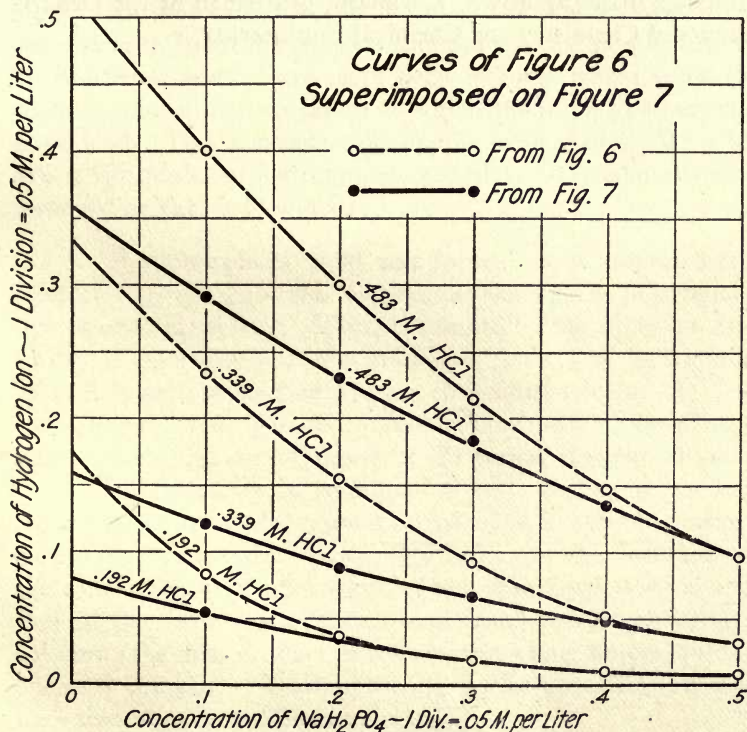
[1] Kolthoff, Pharm. Weekblad **57**, 474 Chemical Abstracts, Volume 14 No. 20, 3011.

must be some concentration of hydrogen ion where there would occur neither an increase nor a decrease for each initial sodium monometaphosphate solution. From data in tables 14 and 16 figures 4 and 5, curves Z and S, for a .3 M. NaPO$_3$ solution this concentration of hydrogen ion must lie between 3.62 x 10^{-4} and 4.18 x 10^{-5} moles per liter. At these initial hydrogen ion concentrations the influence of the concentration of sodium monometaphosphate upon the rate of hydration could be accurately studied without a change of hydrogen ion.

The curves appearing in this article were prepared from tracings made by Mr. S. J. Ballard, draftsman of the Departments of Chemistry and Chemical Engineering.

SUMMARY

1. A definite polymer, sodium monometaphosphate, has been prepared and its hydration studied. A twofold method was employed to follow the hydration; first, the amount transformed to the orthophosphate was separated and determined as orthophosphate by the standard magnesium ammonium phosphate method, second, the hydrogen ion concentration was measured concurrently with the determination of orthophosphate.

2. The hydrogen ion concentration decreased progressively with time except in the .3 Molar $NaPO_3$ solution where the hydrogen ion of the aqueous solution was not supplemented by additional acid. Here there is an increase which tends to reach a point in concentration to which the higher concentrations tend. This concentration lies between 4.18×10^{-5} and 3.62×10^{-4} Moles of hydrogen ion per liter, experimentally determined in Tables 14 and 16.

3. Pyrophosphoric Acid was formed as an intermediate product. Its presence was established during the determination of orthophosphate. It was confirmed by the abnormal decrease of hydrogen ion in solutions in process of hydration. That it is an intermediate product is indicated from: (1) abnormalities of hydrogen ion concentration shown in phosphate-hydrochloric acid curves, figure 9; (2) period of apparent inhibition; (3) tendency in solutions of very low hydrogen ion concentration to exhibit a point of inflection in their hydration curves, experimentally shown, figure 5; (4) the increase of the concentration of hydrogen ion in aqueous solutions above that of the same concentration of a mono-sodium phosphate solution (the final product of the reaction) long before the reaction is complete. This apparently settles a question in dispute since the time of Graham in 1833.

4. The times required for complete hydration for a .5 M. $NaPO_3$ solution with .483 M., .339 M., and .192 M. HCl were 185, 365, and 975 hours respectively. For a .3 molar solution

of NaPO₃ the times required respectively for completion with .339 M., .010 M., and .000 M. HCl were 260 hours, 175 days, and 200 days for 49.14% hydration—a fact which indicates several years for completion.

When the initial concentration of hydrochloric acid was .339 M. in each case the times required to complete the reaction were, respectively, for a .5 M., .3 M., and a .1 M., NaPO₃, 365, 260, and 70 hours.

Seven different hydrations were run in all. Duplicates were obtained from the five which ran rapidly, and duplicate samples were taken in the very slow ones. The seven represent 3 different NaPO₃ concentrations and 4 different initial HCl concentrations.

5. The decrease of hydrogen ion caused jointly by the orthophosphate and pyrophosphate complicates the reaction. From the conduct of the solutions in which hydration occurred the reaction seems to take place in two stages, the first of which is effected more by hydrogen ion. The behavior of solutions of very low hydrogen ion concentration in exhibiting a tendency to show a point of inflection and those of higher hydrogen ion concentration to show a period of apparent inhibition in their respective hydration curves seems to indicate that these reactions are consecutive and not concurrent. The hydration of sodium monometaphosphate is, therefore, by molecular formula, expressed:

$$2NaPO_3 + H_2O \rightarrow Na_2H_2P_2O_7 + H_2O \rightarrow 2NaH_2PO_4 .$$
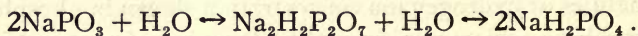
VITA.

Samuel J. Kiehl was born in Sewickley Township, Westmoreland County, Pennsylvania, May 16, 1883. He graduated from Otterbein College, Westerville, Ohio, in 1910, where he taught the year before and the three years following graduation. In 1913 he began teaching in the West High School, Columbus, Ohio. He left West High School in 1917 to become an instructor in the Department of Chemistry, Columbia University, a position he has held to date. While he was teaching in Otterbein and Columbus he was a graduate student at the Ohio State University. He was a graduate student in the Department of Chemistry, Columbia University, during the summers of 1915, 1916, and 1917, and during the years 1917-18, 1918-19, 1919-20, and 1920-21.